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Mixtures and Its Application to the Isotopes on Neon

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A METHOD FOR THE SEPARATION OF GASEOUS ISOTOPE  
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SUMMARY

The process utilizes diffusion through a porous wall into a vacuum. This makes possible the simultaneous action of a great number of diffusion cells and therewith an extensive separation of an isotope mixture in a single operation. The constructed apparatus, consisting of 24 pumps and 48 clay pipes, yields a change in the isotope ratio by almost a factor of 8 in single application on the isotopes of neon within a few hours. Through repeated application a more extensive separation is possible. Mass-spectra and optical-spectra of neon-isotope-mixtures of different composition are re-produced.

The method subsequently described for the separation of isotope mixtures utilizes diffusion through a porous wall into a vacuum, as it was first used for this purpose by Aston, and since then in various ways by Harkins and his collaborators. (F. W. Aston, Phil. Mag. 39, 449, 1920; W. D. Harkins and R. E. Hall, Journ. Amer. Chem. Soc. 38, 53, 1916; W. D. Harkins and C. E. Broeker, Nature 105, 230, 1920; J. N. Bronsted and G. v. Hevesy, ZS. f. phys. Chem. 99, 189, 1921; W. D. Harkins and A. Hayes, Journ. Amer. Chem. Soc. 43, 1803, 1921; R. S. Mulliken, same 45, 1592, 1923; W. D. Harkins and F. A. Jenkins, same 48, 58, 1926; D. D. Harkins and B. Mortimer, Phil. Mag. 6, 601, 1928.)

Since the diffusion velocities for different gases behave themselves as the roots from the molecular weights, a single diffusion process in the case of isotopes will yield only a very slight change in the concentration ratio. Thus, an actual separation of the isotopes has not been attained up to now, but only a relatively small change of the atomic weight, which in the experiments of Harkins in the case of chlorine attained the amount of 0.1.

In order to attain an extensive separation in a short period of time, it was necessary to utilize a large number of diffusion cells simultaneously. This was achieved by constructing the apparatus from a series of separating units, of which each possesses the property to decompose a gas mixture, introduced in a steady stream, into two equal component currents of different composition. Such a separating unit may in the simplest case consist of a pipe with a porous wall (subsequently denoted as clay pipe) as represented in Figure 1. The gas mixture consisting of two components enters at A. One part diffuses through the wall of the pipe and is sucked off at B by a pump which maintains the vacuum in the space surrounding the clay pipe. The remainder of the gas mixture leaves at D. If care is taken to see that exactly one half of the gas entering at A is sucked off at B, the entering gas stream will be decomposed into two component currents, of which the one leaving at B contains the lighter fraction, and the one at D the heavier fraction. A disadvantage of this simple arrangement is the fact that the mixture on the inside of the clay pipe already is so strongly enriched with the heavy fraction, that the mixture diffusing through the wall at the left end of the pipe has almost the same

composition as the original. Therefore, a separating unit was used, as schematically represented in Figure 2. Here the mixture flows successively through two clay pipes. Only the gas which diffuses through the wall of the first clay pipe is sucked off at B as the lighter fraction component current. The remaining gas mixture flows, for further concentration with the heavier fraction, through the clay pipe S and leaves as the second component current at D. The gas which diffuses through clay pipe S is sucked off at C by pump P and returned to A where it once again enters the current.

Such separating units may be connected in parallel in any desirable number. This is done in such a way that each separating unit receives gas from both its adjacent units, and gives off again to the two adjacent units the two component currents, into which it decomposes the received gas. Figure 3 shows the diagram of an apparatus consisting of four separating units.

4 Separating Unit

3 Separating Unit

2 Separating Unit

1 Separating Unit

Figure 3

It also shows in 1/10 of the actual size a picture of the arrangement and the dimensions of the separating units as used in the

apparatus consisting of 24 separating units. The individual separating units are marked off from each other by dotted lines. The letters used in the third unit correspond to those of Figure 2. The gas entering at A into the clay pipe R of the third unit, is decomposed into a lighter fraction, which is sucked off at B by pump  $P_1$ , into a part diffusing through pipe S which is sucked off at C and returned by pump  $P_3$  to A, and into a heavier fraction which flows off at D to the second unit at the left. Regulatory installations are unnecessary since under the action of the pumps the current regulates itself so, that each of these component currents is almost one-third of the gas current entering into pipe R at A. Since in a stationary state the same quantity of gas must flow from one separating unit to the next, just as in the reversed direction, the gas quantity at A, originating from the fourth separating unit, and which flows to the third unit, must be equal to the quantity sucked off at B. Since the pressure, and in the case of isotope mixtures also the composition, change very little from one separating unit to the next, the quantity flowing off at D to the second unit, must also be very nearly equal to the quantity sucked off at B. But this quantity, because of the equal clay pipe lengths, is again equal to the quantity sucked off at C and returned to A. Thus each of the three component currents receives  $1/3$  of the gas entering into pipe R at A.

Both ends of the apparatus are schematically represented in Figure 3. Since no further adjacent units are available to the end units, the gas which actually should be given off to the next adjacent, is here returned to the end unit through a storage container. This makes possible the formation of a stationary state which is essential for the process. The clay pipe to the left of the first separating unit does not act as a separating cell, but only causes the gas to circulate through the end container with the proper velocity.

We may completely neglect further details concerning the operation of the apparatus, and consider only the fact that each separating unit decomposes the gas which it receives into two components, of which the one is the lighter and the other the heavier fraction of the mixture. As will be shown later, these two constituents differ in the concentration ratio of their components by a constant factor  $q$ , which for example has a value of 1.092, in the case of neon. In Figures 4 and 5, the individual separating units are schematically represented by means of squares. The arrows indicate the direction of the current. Each separating member receives gas from both sides, and gives off to the two adjacent units the separated constituents. At the ends, the gas flows through the storage containers. Two cases are readily visualized, namely the initial state when the apparatus is started, and the stationary end state. In the initial state (Figure 4), the same mixture is present everywhere. As a result thereof, the same processes take place in all the separating units. Each separating unit gives off lighter mixture to its right adjacent

unit and heavier to its left. In the figure the lighter mixture is marked by a dotted line and the heavier by a solid line. One recognizes that through the entire apparatus two currents flow towards each other, of which the one predominantly moves the lighter constituent toward the right, and the other predominantly the heavier one toward the left. This state is disturbed due to the change in concentrations in the end containers. Intermediate states, which are difficult to overlook, result in a stationary end state in an asymptotic fashion. In this stationary state the transport from separating unit to separating unit for each individual constituent of the mixture must be equal to zero, that is, the same mixture must flow from one separating unit to the next as in the reversed direction. Since the condition remains that the two component currents which leave one separating unit differ by a certain factor  $q$  in their concentration ratio, the state represented in Figure 5 now results. In this figure the concentration ratio is indicated by the relationship of the dotted line and intermediate space between the lines representing the current. The total current now consists of a series of adjacent circular currents, and the concentration ratio changes from circular current to circular current by the factor  $q$ . Therefore, in the stationary end state, gas mixtures, whose concentration ratios differ by the factor  $q^m$  where  $m$  is the number of separation units, are found in the two end containers  $V_s$  and  $V_l$ .

The proper selection of clay pipes was essential for the practical performance of the process. Their surface area and porosity must fit the output of the pumps that were used.

Furthermore, their inside diameter must not be too great to avoid a radial concentration drop on the inside of the pipe, and not too small so that the pressure drop as a result of the current through the pipe will not be too great. Pipes made from "Q-5 mass" by the Steatit-Magnesia A.-G. proved to be extremely well suited.

"Q-5 mass" is a kaolin-rich, fine fireproof clay. (I express my sincere thanks to the Steatit-Magnesia A.-G for the use of the required pipes.) The pipes used were 30 centimeters long, had an inside diameter of 5 millimeters and a wall thickness of 1 millimeter. The mass is very fine-porous and has the very great advantage that the pipes may be sealed into ordinary glass with the help of sealing glass. Mercury vapor ejectors Model I by Hanff and Buest were used as pumps. These pumps are mounted on a wooden frame. The diffusion apparatus is connected to the pumps by picein-cemented ground sections and is held by the pumps in the manner depicted in Figure 3. Suitable cock connections at the ends enable the insertion of selective containers of different size into the end circles for  $V_s$  and  $V_1$ . In addition, provisions are made for evacuating the apparatus and to draw off the obtained gas into containers with the help of a vapor ejector and a Töpler pump.

After preliminary experiments with neon-helium mixtures in an apparatus of four separating units were successful, the apparatus with 24 separating units was set up in two parallel rows of 12 units each, so that the two ends are close together. The pumps are heated with gas. The water coolings of six pumps each are connected in series. A safety device, as described



recently by W. Pupp, disconnects gas and water independently as soon as something goes wrong with the cooling water supply or if the pressure in the apparatus rises above 20 millimeters Hg. (W. Pupp, Phys. ZS. 33, 530, 1932.) The pressure in the apparatus normally is 10 millimeters Hg. in the end container  $V_1$ . At higher pressure the pump velocity of individual pumps is no longer sufficient. As a result of the pressure drop in the pipes, a pressure difference of 2.5 millimeters Hg. exists between  $V_1$  and  $V_s$ .

Experiments with neon were made to test the apparatus. Normal neon-helium mixture was used as the original material. (Neon-helium mixture was provided for me by the Linde-Corporation and by the Griesheim-Autogen-Sales Corporation for which I express my sincere thanks.) Since in the stationary state a definite ratio of the isotope relationships in the two end containers occurs, a mixture will be found in  $V_1$ , with equal size of the containers, which is filled with the lighter isotope in comparison to the original gas, and in  $V_s$  one which filled with the heavier one. If one wishes to obtain a possible large change of the isotope ratio in comparison to the original one, then either  $V_s$  or  $V_1$  must be chosen possibly large and the other container small. The composition will then change only little in the larger container, and a change of the isotope ratio by almost the entire separation factor of the apparatus will be obtained in the smaller one. In cases where the one isotope is present in only extremely small quantities, such as with oxygen or even to a greater degree with hydrogen, the normal composition in the one end container must be

maintained by permitting fresh gas from the outside to circulate continuously through the end volume.

During the first experiments with neon a container composed of six glass spheres with a capacity of 30 liters was used for  $V_S$ , and for  $V_1$  a similar one of 5 liters. After the apparatus was filled with neon-helium mixture, pure helium first collected in  $V_1$ . After the greatest part of the helium was removed in this manner, the 30 liter container was inserted as  $V_1$ , and a volume of about 400 centimeters<sup>3</sup> used as  $V_S$ . After the apparatus was in operation in this connection for 8 hours, the contents of  $V_S$  were pumped off for examination. (Subsequent experiments showed that the end state with this size of  $V_S$  is already attained after 4 hours). In order to obtain a fraction enriched with the lighter isotope, the two containers were exchanged. After the helium which was still collecting in  $V_1$  was pumped off, the apparatus was put into operation for 8 hours again, and then the content of  $V_1$  removed.

A mass spectrograph based on the Thomson parabola method was used to examine the composition of the fractions obtained by the above method. (The mass spectrograph was constructed by Diploma-Engineer H. Lukanow as part of his diploma fulfillment.) Figure 6 shows the mass spectra of the fractions obtained by a single separation in the manner described above. On the spectrum of the lighter fraction, the isotope 22 is recognized with extreme difficulty, while the one of the heavier fraction shows both isotopes in approximately equal intensity. For comparison,

Figure 7 shows the mass spectrum of normal neon.

Figure 7: Normal Neon

The mass spectra are of little value for a quantitative determination of the isotope ratio, because of the unfavorable form of their characteristic film curve. In the case of neon it is more convenient to observe the optical spectrum, in which the isotopic fine structure was found by G. Hansen. (G. Hansen, *Naturwissenschaften* 15, 163, 1927.) In Figures 8 to 11 plates are reproduced of the spectra of different fractions, taken with the help of a Perot-Fabry-standard instrument at 44 millimeters plate distance (6143 to 6402 Ångstroms). (I am obliged to Dr. F. Houtermans for the taking of these spectra.)

Figure 8: Normal Neon

Figure 8 shows the spectrum of normal neon. The isotopic fine structure is noticeable by means of a weak short-waved indicator, which is identifiable on the photograph only in the case of the heavier lines. Figure 9 shows the spectrum of a fraction in which the isotope 22 is no longer optically detectable; Figure 10 one of a mixture which contains the two isotopes in exactly equal quantity; Figure 11 one of a mixture with the isotope ratio  $\text{Ne}^{20} : \text{Ne}^{22} = 1:2.5$ . This ratio is estimated by comparison of the densities with those of an intensity scale photographed on the same plate. The two last fractions were obtained by using the

process twice, since only about the ratio 10:8 is obtained if the process is used once.

In order to follow the periodic course of the separation process, suitable spectral tubes were connected to the two end containers for the observation of the fine structure. (An interference plate generously made available by the Halle Company was used for observing the fine structure.) By use of a volume of 400 centimeters<sup>3</sup> for  $V_s$ , the equilibrium state was attained after 4 hours. Since the gas pressure in  $V_s$  is a maximum of 7.5 millimeters Hg, a quantity of 4 centimeters<sup>3</sup> is obtained from atmospheric pressure during this time.

A parabola, corresponding to the mass 23, is always present on the mass spectra of the heavy fractions, in addition to the isotope 21, when sufficient lighting is available. Experiments with further concentration will have to decide whether another neon isotope is involved.

It is intended to increase the apparatus in order to increase the degree of separation with a single application of the process to such an extent, that the separation or concentration, of the isotopes of hydrogen, oxygen (in form of water vapor), nitrogen ( $NH_3$ ), and chlorine ( $HCl$ ) may be undertaken with the possibility of success. It should also be investigated whether a change in the structure of the apparatus would also increase its efficiency. To get a picture of the quantitative relationships, a single separating unit will be considered as represented in Figure 12. The glass pipe between the two clay

pipes R and S has been omitted, so that the two clay pipes are combined into one, of which however the parts R and S are located in separate, vacuum spaces. In contrast to the existing installation, the diagram is generalized insofar as pipes R and S are no longer of equal length. The letters in the diagram correspond to those in Figures 2 and 3. Here also the gas quantity flowing from B to the right separating unit per unit of time, will be equal to the one flowing from D to the left unit, as a result of the linkage with the neighbor units. While, however, in the existing arrangement the gas entering at A left, at B and D in the quantity of  $1/3$  at each point, here it will be a different fraction which we will call  $f$ . As is readily seen,  $f$  depends only on the ratio of the lengths of the two clay pipes. Thus  $\frac{1}{f} = \frac{l_s}{l_r} + 2$ , where  $l_r$  and  $l_s$  are the lengths of the two pipes.

In order to estimate the maximum attainable degree of separation and the velocity of the separation, we will calculate the composition of the component currents which leave at B and D, with a given composition of the gas entering at A. To simplify the calculation, we limit ourselves to the special case of an isotope mixture of only two components, of which the heavier one is present in only a small quantity. From the lighter isotope,  $n_0$  molecules will enter into the clay pipe at A in the unit time, and from the heavier one  $V_0 = c_0 \cdot n_0$ , where the concentration  $c_0$  is assumed as being small near 1. Since the fraction  $f$  is pumped off through the wall of R, in the unit time  $n, n_1 = n_0 (1 - f)$  molecules of the heavier components will pass point E and enter

pipe S. Of these  $n_2 = n_0 \cdot f$  will reach the left end of S and will leave at D. Since the heavier molecules will diffuse slower through the wall, corresponding to the ratio of the roots of the molecular weights, the concentration  $c$  within the clay pipe will increase from right to left. If we assume a host of molecules of the mixture which enter at A at the time  $t = 0$ , the number of molecules belonging to this host for each of the two components, will decrease exponentially during passage through the clay pipe, since the number of molecules which leave in the unit time by diffusion through the pipe wall is proportional to the number present. If the number of the lighter molecules decreases according to the law  $N = N_0 e^{-\alpha t}$  then  $cN = c_0 N_0 e^{-\mu \alpha t}$

will be valid for the heavier ones, where  $\mu = \sqrt{\frac{m_l}{m_s}}$  and  $m_l$  or  $m_s$  are the molecular weights of the lighter or heavier component. For concentration  $c$  this will yield

$$c = c_0 \left( \frac{N}{N_0} \right)^{\mu-1}$$

If we neglect the diffusion in the gas in the longitudinal direction of the pipe, we may substitute  $N/N_0$  by  $n/n_0$ . The concentrations:

$$c_1 = c_0 (1-f)^{\mu-1}; c_2 = c_0 f^{\mu-1}$$

result for points E and D, and therefore for the number of molecules of the heavier component flowing past in the unit time.

$$v_1 = c_0 n_0 (1-f)^{\mu}; v_2 = c_0 n_0 f^{\mu}$$

The number of molecules of the heavy isotope which are sucked off at B in the unit time is

$$v_L = v_0 - v_1 = c_0 n_0 (1 - (1-f)^{\mu})$$

The number of those leaving at D in the unit time is:

$$V_s = V_2 = c_0 n_0 f^M$$

Since equal quantities of the lighter molecules leave at B and D under the assumption  $C < 1$  which was made, we obtain for the ratio of the concentration of the heavier component in the two component currents, which leave the separating unit under consideration, the value:

$$q = \frac{V_s}{V_l} = \frac{f^M}{1 - (1-f)^M}$$

If the total apparatus has  $m$  separating members, then there will result for the separating factor, that is for the ratio of the concentrations in the two end containers in the stationary state, the value:

$$Q = \left( \frac{f^M}{1 - (1-f)^M} \right)^m \quad (1)$$

In the apparatus used up to now,  $f = 1/3$ ,  $u = 0.953$  for the neon isotopes, and  $m = 24$ . Substitution of these values yields  $Q = (1.092)^{24} = 8.4$ . The actual attained separation degree has not yet been measured exactly. In any case, it will not be more than 20 percent less than the calculated value.

In addition to the separation factor  $Q$ , the magnitude:

$$V_s - V_l = c_0 n_0 [f^M - 1 + (1-f)^M] = c_0 n_0 G \quad (2)$$

is of significance for the practical application of the process,

since it indicate the velocity with which at the start the heavy isotope is transported through the apparatus. It is proportional to the concentration, the intensity of the gas current, and the magnitude:

$$Q = f^M + (1-f)^M - 1 \quad (3)$$

which may be denoted as the relative separation velocity.

In Figure 13, the magnitudes  $Q$  and  $G$  are represented as a function of the magnitude  $f$ , which is depended on the length ratio of the pipes, for an apparatus of 24 similar separating units and for the case using neon isotopes. The small crosses denote the points  $f = 1/3$  corresponding to the apparatus used up to now. It is seen that by decreasing  $f$ , that is by shortening clay pipe  $R$  and correspondingly lengthening  $S$ , a substantial increase of the separation factor could be attained at the expense of the separating velocity. The increase in the separation factor, which is possible in this manner, is limited in practice by the fact that with a decreasing value of  $f$  the current velocity in the left end of  $S$  will decrease. At a certain limit, the assumption that the diffusion in the gas in the longitudinal direction of the pipe might be neglected, which was made in the calculation, no longer will hold. Below this limit, in the case being considered, the separation caused by the diffusion through the clay pipe will be more or less cancelled again as a result of the diffusion of the heavier isotope compared to the current of the lighter one. Where this



limit is located is to be determined by experiments. It will also be attempted to lessen this influence of the longitudinal diffusion by giving the left end of S a smaller diameter.

Of special interest is the limiting value  $f = 0$ . It leads to an arrangement as represented in Figure 14 for the case of three separating units. Since here the velocity on the left side of each separating unit is zero, the diffusion in comparison to the gas current plays the decisive role. The diffusion limits the separation of the mixture, which during its passage through the clay pipe loses continually more of the lighter than of the heavier part. On the other hand, the diffusion also causes the separation velocity not to become zero, as it would be according to equation (3), since now a gas exchange between neighboring separating units results by diffusion. A preliminary experiment with such an apparatus, consisting of 6 separating units, has already shown that it is at least equivalent to the former one with respect to the degree of separation. The separation velocity, on the other hand, will be smaller. Despite this, it is not impossible that this arrangement may be used advantageously in certain cases because of its simplicity and its smaller volume.

Regarding the velocity with which the separation occurs in an apparatus consisting of a larger number of separating units, the following should be noted: According to equation (2), the velocity with which a component is transported is proportional to its concentration. As a result thereof, the periodic progress of the process in the entire separation apparatus will be determined by the location of the least concentration, thus

by the last separating unit. For the last separating units one would thus select such, which possess a relatively large separating velocity with a moderate separation factor. For those separating units in which in a stationary state, higher concentrations already exist, such should be selected whose separation factor is increased at the expense of the separating velocity.

The execution of the experiments was made possible with funds granted by the Aid Society of German Science, for which I wish to express my gratitude. W. Schutze, professional engineer, provided me with valuable assistance during the construction and operation of the apparatus.

Berlin, Physical Institute of the Technical College,  
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#### CORRECTION

To the paper by G. Hertz: A Method For The Separation Of Isotope Mixtures and its Application to the Isotopes of Neon. (ZS. f. Phys. 79, 108-121, 1932.)

1. On pages 114 and 115 two photographs have been interchanged, so that the figures do not correspond to the text and to the captions. The right photograph of Figure 6 actually shows the mass spectrum of normal neon. The mass spectrum printed as Figure 7 is that of a mixture obtained as a heavier fraction by a single application of the separation process, and which contains the two isotopes in approximately equal quantity.

2. On page 118 the last word of the 19th line, namely, "heavier", is to be replaced by "lighter".